



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 338 529
A2

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 89107024.5

⑭ Int. Cl.4: C08G 65/00, C10M 147/04,
C10M 145/38

⑮ Date of filing: 19.04.89

⑯ Priority: 19.04.88 JP 97681/88

⑰ Date of publication of application:
25.10.89 Bulletin 89/43

⑱ Designated Contracting States:
DE FR GB

⑲ Applicant: DAIKIN INDUSTRIES, LIMITED
Umeda Center Building 4-12, Nakazaki-nishi
2-chome Kita-ku
Osaka-shi Osaka-fu(JP)

⑳ Inventor: Tohzuka, Takashi
1-5-9-401, Wakayamadal Shimamoto-cho
Mishima-gun Osaka-fu(JP)
Inventor: Yamamoto, Ikuo
4-11-11, Tezukayama-naka Sumiyoshi-ku
Osaka-shi Osaka-fu(JP)
Inventor: Misugi, Yoshihiko
10-6, Kurakuen 4-bancho
Nishinomiyasho Hyogo-ken(JP)

㉑ Representative: Hansen, Bernd, Dr.rer.nat. et
al
Hoffmann, Eitie & Partner Patentanwälte
Arabellastrasse 4 Postfach 81 04 20
D-8000 München 81(DE)

㉒ Fluorine-containing polyether and lubricant comprising the same.

㉓ A fluorine-containing polyether of the formula:

R₁'COOR₂ (I)

or

R₂'OCO-R₁'-COOR₂ (II)

wherein R₁' and R₂' are a group containing a per-fluoroalkyl polyether group, and R₂' is a fluorine-containing alkyl group or a fluorine-containing ether group.

can be used as a lubricant which has good properties such as lubricity and durability.

EP 0 338 529 A2

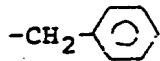
FLUORINE-CONTAINING POLYETHER AND LUBRICANT COMPRISING THE SAME.

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to a novel fluorine-containing polyether and a lubricant comprising the same fluorine-containing polyether.

Description of the Related Art

A perfluoropolyether is a fluorine-containing oil which has non-flammability and good durability. However, the perfluoropolyether has a weak affinity to a surface of a material such as a metal or a glass. When it is thinly spread, for example, on a metal surface and used as a lubricant, it has such a problem that durability is very poor because of migration. To solve the problem of the perfluoropolyether, a fluorine-containing polyether which has, at an end of the molecule, -COOH, -CH₂OH or -COOR wherein R is -CH₃ or



has been developed. However, the fluorine-containing polyether has defects that those having the carboxyl group must be carefully treated and properties such as lubricity or durability are insufficient.

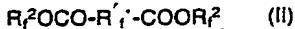
SUMMARY OF THE INVENTION

An object of the present invention is to provide a fluorine-containing polyether which can be easily treated and has good properties such as lubricity and durability.

This and other objects are achieved by a fluorine-containing polyether of the formula:



or



wherein R₁' and R₂' are a group containing a perfluoroalkyl polyether group, and R₂' is a fluorine-containing alkyl group or a fluorine-containing ether group.

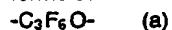
Also, the present invention provides a lubricant comprising said fluorine-containing polyether.

BRIEF DESCRIPTION OF THE DRAWING

Figure is an IR chart of the fluorine-containing polyether of Example 1.

DETAILED DESCRIPTION OF THE INVENTION

In the fluorine-containing polyethers (I) and (II) according to the present invention, the perfluoroalkyl polyether group in the R₁' and R₂' groups contains at least one repeating unit selected from the group consisting of a repeating unit of the formula:

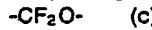


a repeating unit of the formula:



and

a repeating unit of the formula:

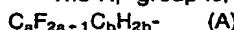


provided that at least one of the repeating units (a) and (b) is contained. Total number of the repeating units (a), (b) and (c) is at least three. The repeating unit: -C₃F₆O-includes -CF₂CF₂CF₂O- and -CF-(CF₃)CF₂O-. The repeating unit: -C₂F₄O- is usually -CF₂CF₂O-.

The R₁' group is, for example, F(CF₂CF₂CF₂O)_mCF₂CF₂- wherein m is 2 to 200.

The R₂' group is, for example, -CF₂CF₂O(CF₂CF₂CF₂O)_n(CF₂)₄(OCF₂CF₂CF₂O)_nOCF₂CF₂- wherein each of n is 2 to 200.

The R² group is, for example,



wherein a is an integer of 1 to 10 and b is 1 or 2,



wherein d is an integer of 1 to 5,

or

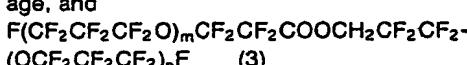


wherein l, m and n are 0 or a positive integer provided that at least one of l and m is not 0 and l + m + n is not smaller than 3. In the fluorine-containing ether group (C), the order of each repeating unit may not be the same as described above and is arbitrary in the molecule.

Specific examples of the fluorine-containing polyether according to the present invention are F(CF₂CF₂CF₂O)_mCF₂CF₂COOCH₂CF₂CF₃ (1) wherein m is 2 to 200, preferably 25 on the average,



wherein m is 2 to 200, preferably 20 on the average, and



wherein m is 2 to 200, preferably 20 on the average and n is 2 to 200, preferably 20 on the average.

The fluorine-containing polyether according to the present invention can be prepared by reacting a fluorine-containing compound of the formula:

R_1^1-COOH ,

$R_1^1-CO_2$, or

$HOOC-R_1^1-COOH$

wherein R_1^1 and R_1^1 are the same as described above, with a fluorine-containing alcohol of the formula:

R_2^2OH

wherein R_2^2 is the same as described above. A catalyst such as an acid (e.g. sulfuric acid) is preferably used in the reaction. The reaction is usually carried out at a temperature of 50 to 150 °C for 1 to 10 hours.

The fluorine-containing polyether according to the present invention can be used as a lubricant for materials such as a metal, a glass, a silica gel and graphite. It is particularly useful as the lubricant for a thin film magnetic tape or a thin film magnetic disc.

A solution of the lubricant is preferably prepared by using a solvent so as to apply the lubricant on the surfaces of various materials. Specific examples of the solvent are a fluorine-containing solvent, for example, trichlorotrifluoroethane (e.g. Daiflon S-3 manufactured by Daikin Industries, Ltd.), $Cl(CF_2CFCl)_2Cl$ and $N(C_3F_7)_3$. The solvent may be used in an amount of 200 to 2000 parts by weight per part by weight of the lubricant.

Then, the solution of the lubricant is applied on a surface of a substrate such a magnetic tape or a magnetic disc by dipping or spraying, and heated to form a lubricant film. The solvent is evaporated by heating. The heating may be usually carried out at a temperature of about 80 °C. The lubricant film may be formed to have a thickness of 0.002 to 0.01 μm .

The reason why the lubricant according to the present invention has good properties such as lubricity and durability is not clearly known. It is assumed that since the metal, glass, silica gel and graphite have many hydroxyl groups on their surfaces, the fluorine-containing polyether is adsorbed on their surfaces because of transesterification between the fluorine-containing polyether and the hydroxyl group. When the fluorine-containing polyether has sufficiently higher acidity than that of the hydroxyl group of the surface, the fluorine-containing alcohol moiety of the fluorine-containing polyether quickly transesterifies with the hydroxyl group of the surface. The transesterification is achieved in the heating process to evaporate the solvent. The transesterification is completed by the frictional heat during use.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention is illustrated by following Examples.

Example 1

In a 200 ml three-neck flask, the fluorine-containing carboxylic acid: $F(CF_2CF_2CF_2O)_pCF_2CF_2COOH$ wherein p is 25 on the average (200 g, 57 mmol) and then pentafluoropropanol (20 g, 130 mmol) were added and stirred. Then, concentrated sulfuric acid (0.5 ml) was added and the reaction was carried out at 90 °C for 5 hours while stirring. The completion of the reaction was confirmed by disappearance of the absorption peak at 1780 cm^{-1} for the carboxylic acid and appearance of the absorption peak at 1820 cm^{-1} for the ester linkage in IR analysis. After the completion of the reaction, the reaction product was washed with water (100 ml) and a lower phase was separated. Silica gel (30 g) was added to the lower phase to remove the unreacted carboxylic acid. The reaction product was filtrated through a filter having a pore diameter of 0.2 μm to obtain the fluorine-containing polyether: $F(CF_2CF_2CF_2O)_pCF_2CF_2COOCH_2CF_2CF_3$ wherein p is 25 on the average. Yield: 300 g (78%).

The IR chart of the resultant fluorine-containing polyether is shown in Figure.

Example 2

To the fluorine-containing carboxylic acid:

$F(CF_2CF_2CF_2O)_qCF_2CF_2COOH$ wherein q is 20 on the average (20 g), the fluorine-containing alcohol: $F(CF_2CF_2CF_2O)_rCF_2CF_2CH_2OH$ wherein r is 15 on the average (15 g) was added and stirred. Then, concentrated sulfuric acid (2 ml) was added and the reaction was carried out at 150 °C for 10 hours while stirring. The completion of the reaction was confirmed by disappearance of the absorption peak at 1780 cm^{-1} for the carboxylic acid and appearance of the absorption peak at 1820 cm^{-1} for the ester linkage in IR analysis. After the completion of the reaction, the reaction product was washed with water (50 ml) three times and a lower phase was separated. Silica gel (100 g) was added to the lower phase to remove the unreacted carboxylic acid. The reaction product was filtrated through a filter having a pore diameter of 0.2 μm to obtain the fluorine-containing polyether:

$F(CF_2CF_2CF_2O)_qCF_2CF_2COOCH_2CF_2CF_2-$
 $(OCF_2CF_2CF_2)_rF$
 wherein q is 20 and r is 15 on the average. Yield:
 24 g (64%).

Example 3

A two patch type hard disc having an uppermost carbon layer was dipped in a 0.1% by weight solution of the fluorine-containing polyether:

$F(CF_2CF_2CF_2O)_pCF_2CF_2COOCH_2CF_2CF_3$
 wherein p is 25 on the average prepared in Example 1 in trichlorotrifluoroethane. The disc was removed from the solution and heated at 80 °C for one hour in an oven. A resultant lubricant film had a thickness of 0.01 μm.

The durability of the hard disc was tested by using a CSS Tester. After 20,000 times, the μ value was not more than 0.5.

Comparative Example

A hard disc was treated in the same manner as in Example 3 but using the perfluoropolyether oil: $F(CF_2CF_2CF_2O)_pCF_2CF_3$
 wherein p is 25 on the average instead of the fluorine-containing polyether. A resultant lubricant film had a thickness of 0.01 μm. After 1,100 times, the μ value exceeded 0.5.

Claims

1. A fluorine-containing polyether of the formula:
 $R'_1COOR'_2$ (I)

or

$R'_2OCO-R'_1-COOR'_2$ (II)

wherein R'_1 and R'_2 are a group containing a perfluoroalkyl polyether group, and R'_2 is a fluorine-containing alkyl group or a fluorine-containing ether group.

2. The fluorine-containing polyether according to claim 1, wherein the perfluoroalkyl polyether group in the R'_1 and R'_2 groups contains at least one repeating unit selected from the group consisting of a repeating unit of the formula:

$-C_3F_6O-$ (a)

a repeating unit of the formula:

$-C_2F_4O-$ (b)

and

a repeating unit of the formula:

$-CF_2O-$ (c)

provided that at least one of the repeating units (a) and (b) is contained and total number of the repeating units (a), (b) and (c) is at least three.

3. The fluorine-containing polyether according to claim 1, wherein the R'_2 group is $C_aF_{2a+1}C_bH_{2b}-$ (A)

wherein a is an integer of 1 to 10 and b is 1 or 2,
 $H(C_2F_4)_dCH_2-$ (B)

wherein d is an integer of 1 to 5,
 or

$F(C_3F_6O)(C_2F_4O)_m(CF_2O)_nCF_2CH_2-$ (C)

wherein l, m and n are 0 or a positive integer provided that at least one of l and m is not 0 and l + m + n is not smaller than three.

4. The fluorine-containing polyether according to claim 1, wherein the R'_1 group is

$F(CF_2CF_2CF_2O)_pCF_2CF_2-$

wherein p is an integer of 2 to 200, and the R'_2 group is $-CH_2CF_2CF_3$.

5. The fluorine-containing polyether according to claim 1, wherein the R'_1 group is

$F(CF_2CF_2CF_2O)_qCF_2CF_2-$

wherein q is an integer of 2 to 200, and the R'_2 group is

$-CH_2CF_2CF_2(OCF_2CF_2CF_2)_rF$

wherein r is an integer of 2 to 200.

6. A lubricant comprising the fluorine-containing polyether according to claim 1.

EP 0 338 529 A2

